Electronic Supplementary Information (ESI)

Synthesis of New Polyesters by Acyclic Diene Metathesis Polymerization of Bio-Based α,ω-Dienes Prepared from Eugenol and Castor Oil (Undecenoate)

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Table of Contents

(i) ^{1}H and ^{13}C NMR spectra for monomers, crosslinker and polymers synthesized by ADMET polymerization

4-Allyl-2-methoxyphenyl 10-undecenoate (M1)

^{1}H NMR ($CDCl_3$): δ 1.33 (s, 10H, 5CH_2) 1.75-1.79 (quint, *J*=7.5 Hz, 2H, CH_2), 2.03-2.07 (quart, *J*=7.5 Hz, 2H, CH_2CH=CH_2), 2.55-2.58 (t, *J*=7.5 Hz, 2H, -CH_2COO-), 3.37-3.38 (d, *J*=6.8 Hz, 2H, Ar-CH_2), 3.81 (s, 3H, OCH_3), 4.92-5.02 (m, 2H, Ar-CH_2CH=CH_2), 5.08-5.13 (2H, -CH=CH_2), 5.78-5.86 (m, *J*=6.68, 6.68 and 6.77 Hz, 1H, -C*H*=CH_2), 5.92-6.0 (m, *J*=6.75, 6.75 and 6.79 Hz, 1H, Ar-CH_2C*H*=CH_2), 6.75-6.79 (m, 1HAr, C*H*), 6.93-6.94 ppm (m, 2HAr, 2C*H*). ^{13}C NMR ($CDCl_3$): δ 25.1 (*C*H_2), 29.0 (*C*H_2), 29.1 (*C*H_2), 29.3 (*C*H_2), 29.4 (*C*H_2), 33.9 (*C*H_2COO-), 34.1 (*C*H_2), 40.2 (Ar-*C*H_2), 55.9 (O*C*H_3), 112.8 (*C*H), 114.3 (CH=*C*H_2), 116.2 (Ar-CH_2CH=*C*H_2), 120.7 (*C*H), 122.6 *C*H), 137.2 (Ar-CH_2*C*H=CH_2), 138.2 (*C*), 138.9 (*C*), 139.3 (*C*H=CH_2), 151.0 (*C*), 172.1 ppm (-*C*OO-).

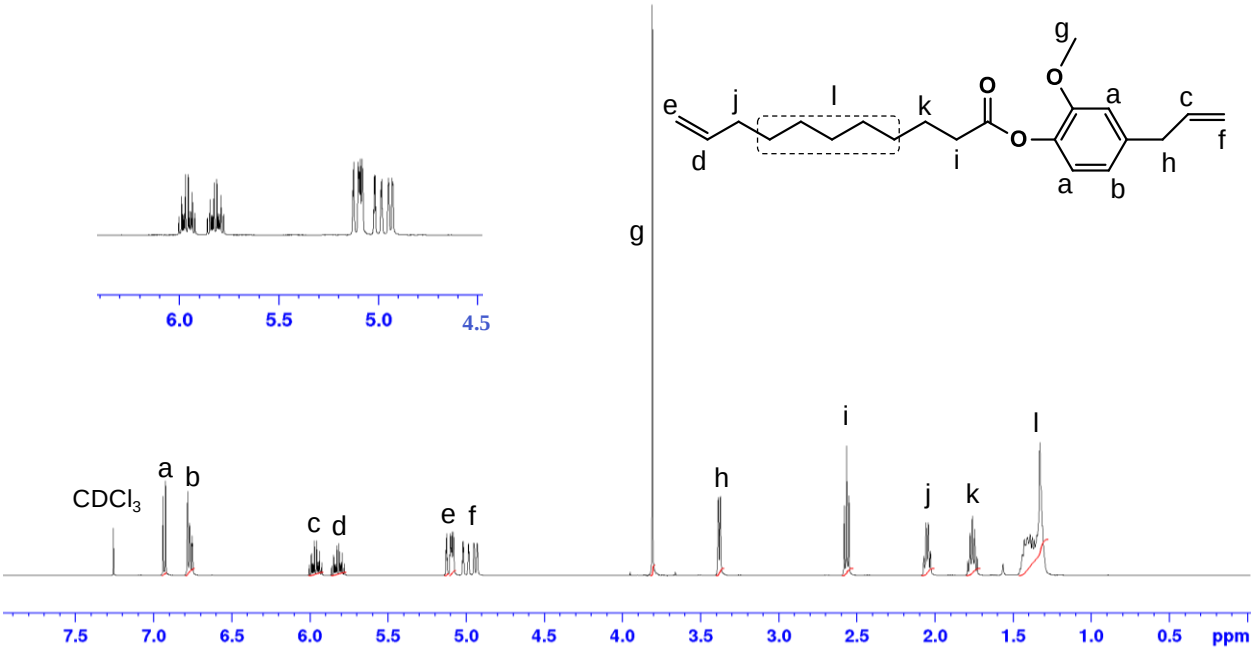

Figure S1. ^{1}H NMR spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (**M1**)

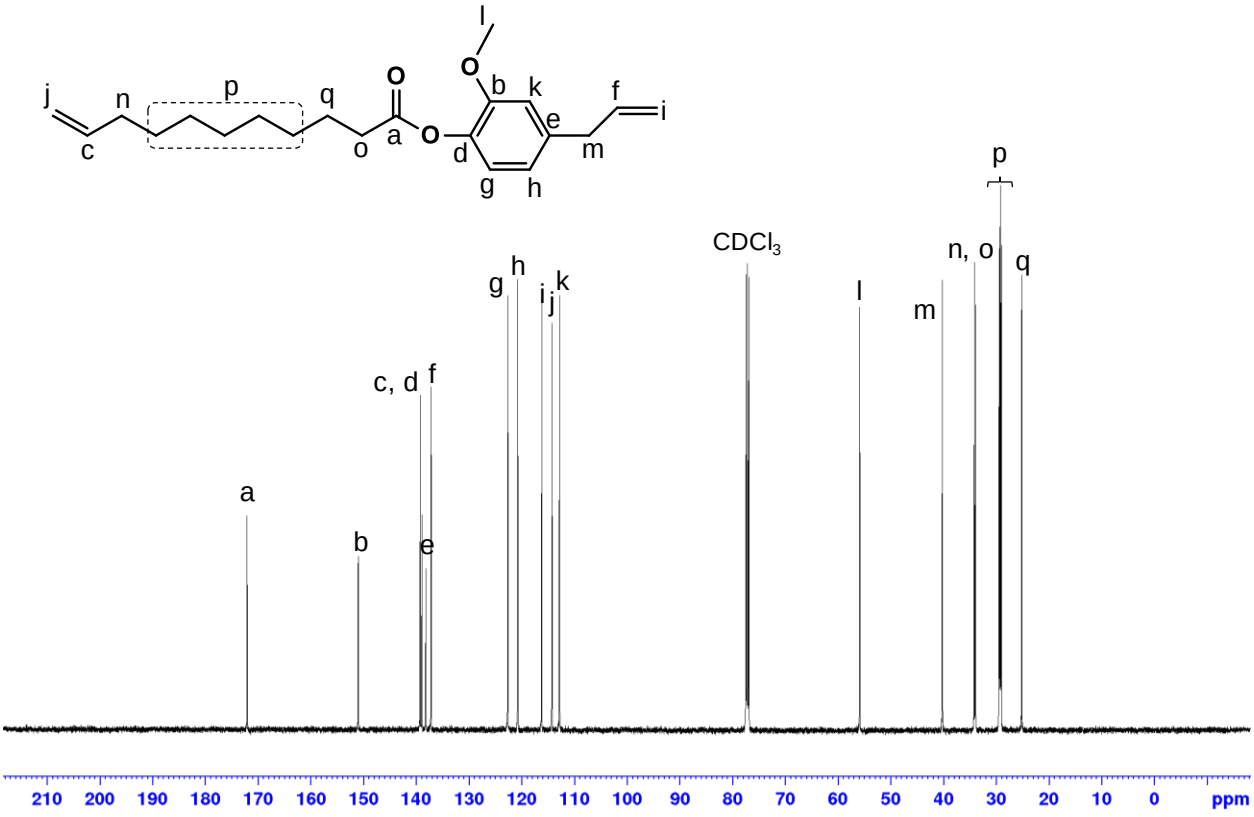

Figure S2. ^{13}C NMR spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (**M1**)

5-Hexen-1-yl 10-undecenoate (M2)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.28-1.36 (s, 10H, 5C*H*$_2$), 1.44 (m, 2H, C*H*$_2$), 1.61-1.64 (m, 4H, 2C*H*$_2$), 2.02-2.08 (m, *J*=15.2 and 16.9 Hz, 4H, 2C*H*$_2$CH=CH$_2$), 2.26-2.29 (t, *J*=7.4 Hz, 2H, -C*H*$_2$COO-), 4.06 (t, *J*=6.5 Hz, 2H, -COOC*H*$_2$-), 4.91-5.02 (m, *J*=8.8 and 14.0 Hz, 4H, 2C*H*$_2$=CH-), 5.77-5.80 ppm (m, *J*=1.4 and 11.6 Hz, 2H, 2CH$_2$=C*H*-). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 25.1 (*C*H$_2$), 25.3 (*C*H$_2$), 28.2 (*C*H$_2$), 29.0 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 33.4 (*C*H$_2$), 33.9 (*C*H$_2$), 34.5 (*C*H$_2$), 64.2 (-COO*C*H$_2$-), 114.3 (CH=*C*H$_2$), 139.3 (*C*H=CH$_2$), 174.1 ppm (-*C*OO-).

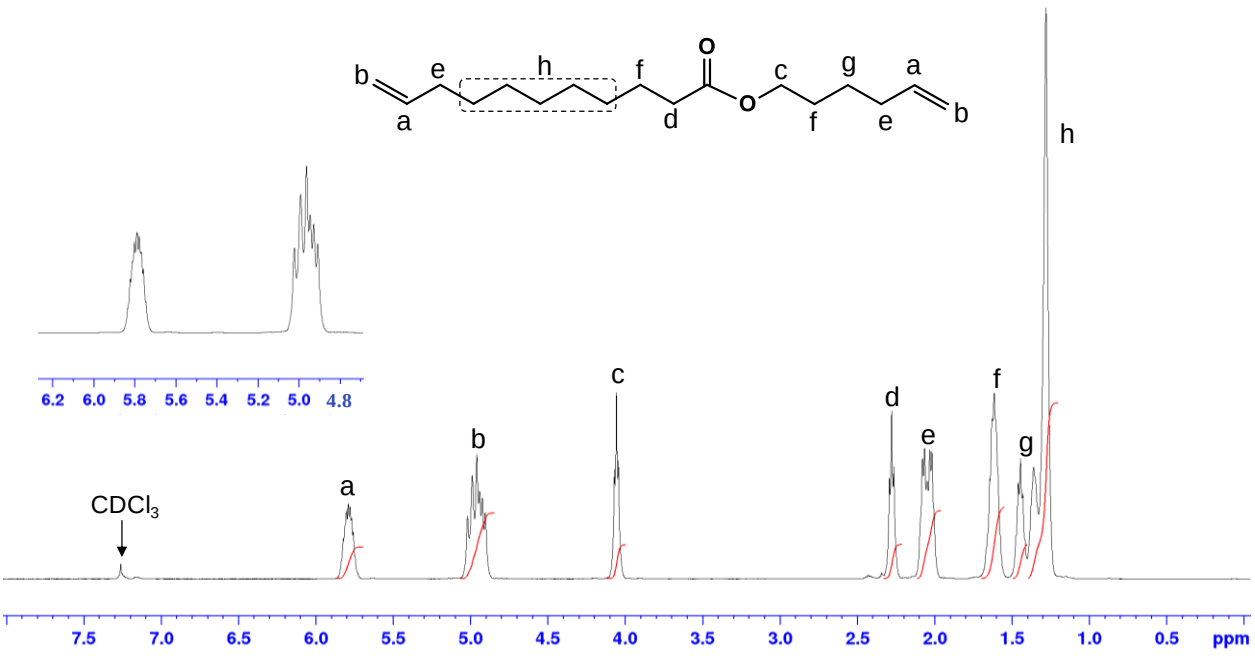

Figure S3. ^{1}H NMR spectrum of 5-hexen-1-yl 10-undecenoate (**M2**)

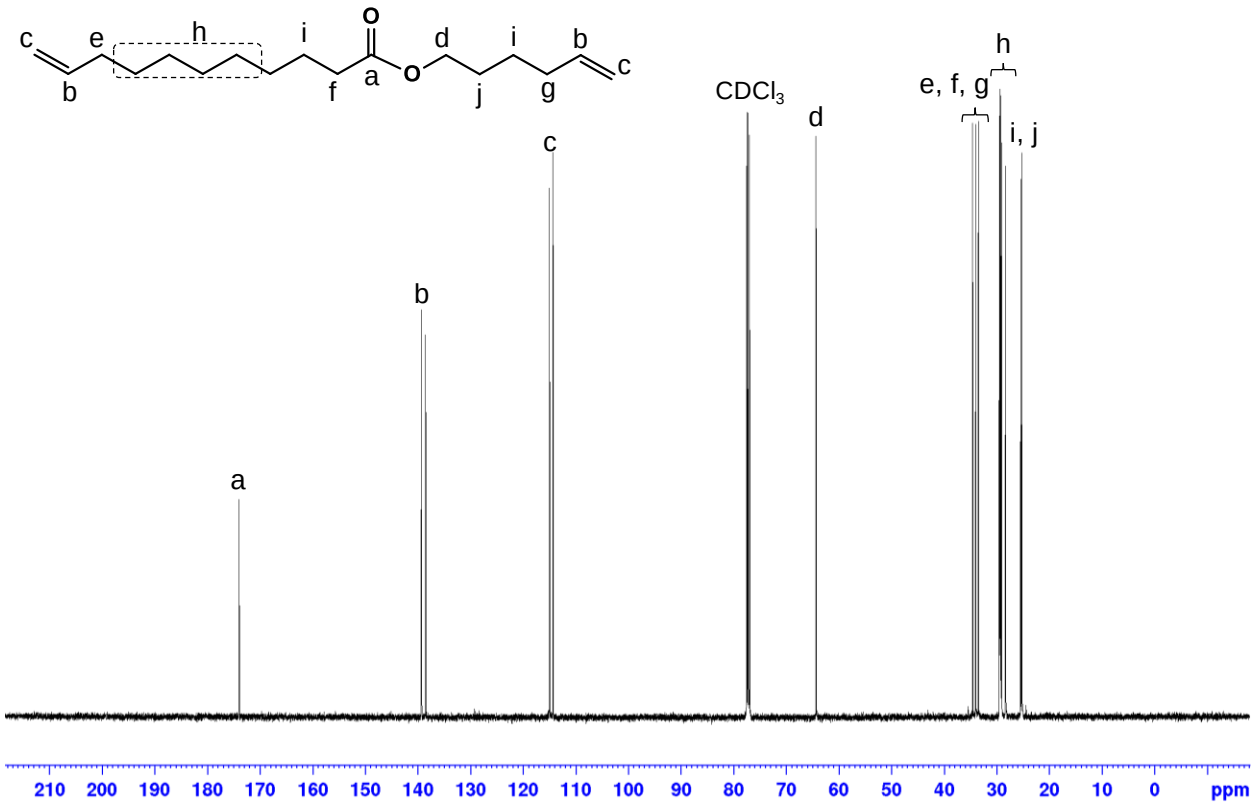

Figure S4. ^{13}C NMR spectrum of 5-hexen-1-yl 10-undecenoate (**M2**)

10-Undecen-1-yl 10-undecenoate (M3)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.27-1.36 (s, 22H, 11CH_2), 1.60 (s, 4H, 2CH_2), 2.02-2.03 (d, *J*=6.4 Hz, 4H, 2CH_2CH=CH_2), 2.26-2.29 (t, *J*=7.4 Hz, 2H, -CH_2COO-), 4.03-4.05 (t, *J*=6.6 Hz, 2H, -COOCH_2-), 4.90-4.99 (m, *J*=9.3 and 17.1 Hz, 4H, 2CH_2=CH-), 5.76-5.81 ppm (d, *J*=6.8 Hz, 2H, 2CH_2=C*H*-). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.0 (*C*H_2), 28.8 (*C*H_2), 29.0 (*C*H_2), 29.1 (*C*H_2), 29.2 (*C*H_2), 29.3 (*C*H_2), 29.4 (*C*H_2), 29.5 (*C*H_2), 29.6 (*C*H_2), 33.9 (*C*H_2), 34.5 (*C*H_2), 64.5 (-COO*C*H_2-), 114.2 (CH=*C*H_2), 139.2 (*C*H=CH_2), 174.0 ppm (-*C*OO-).

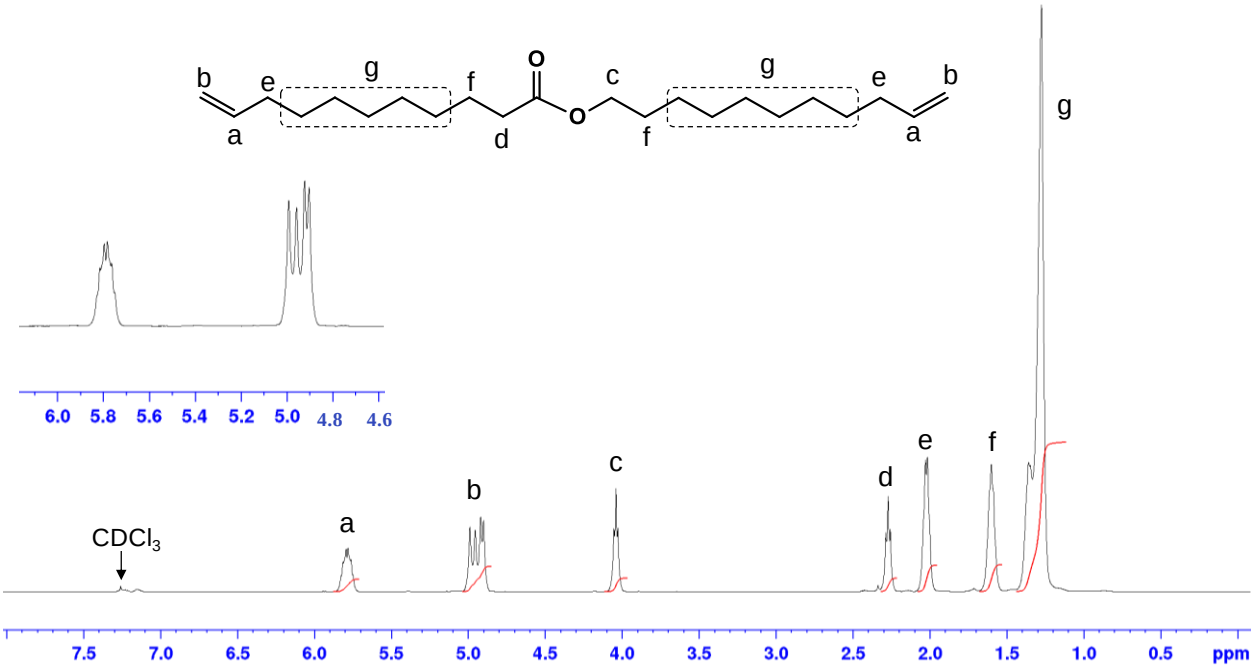

Figure S5. ^{1}H NMR spectrum of 10-undecen-1-yl 10-undecenoate (**M3**)

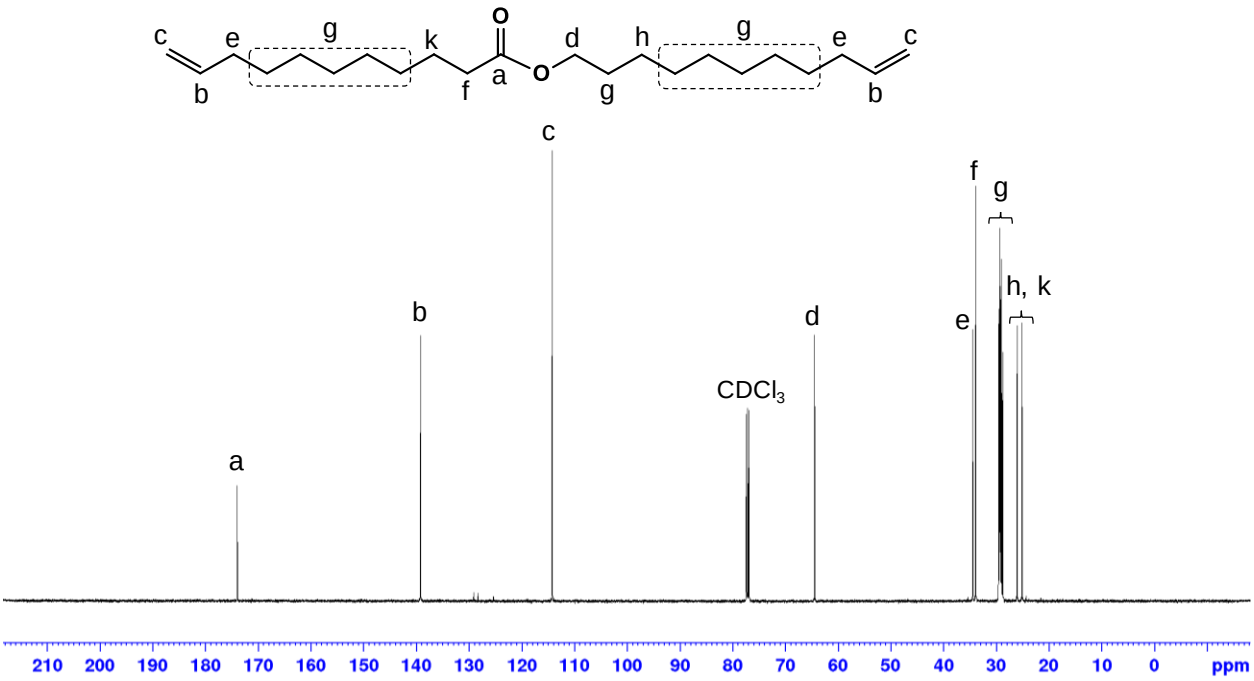

Figure S6. ^{13}C NMR spectrum of 10-undecen-1-yl 10-undecenoate (**M3**)

5-Formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)

^{1} ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.32-1.40 (s, 30H, 15C*H*$_2$) 1.70-1.76 (quint, *J*=7.5 Hz, 6H, 3C*H*$_2$), 2.02-2.06 (quart, *J*=7.0 Hz, 6H, 3C*H*$_2$CH=CH$_2$), 2.53-2.56 (t, *J*=7.5 Hz, 6H, 3C*H*$_2$COO-), 4.92-5.01 (m, *J*=10.2 and 17.1 Hz, 6H, 3CH=C*H*$_2$), 5.77-5.85 (m, *J*=16.7, 16.8 and 17.0 Hz, 3H, 3C*H*=CH$_2$), 7.64 (s, 2HAr, 2C*H*), 9.92 ppm (s, 1H, -CO*H*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 24.9 (*C*H$_2$), 29.0 (*C*H$_2$), 29.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 33.8 (*C*H$_2$), 114.3 (CH=*C*H$_2$), 121.7 (*C*H), 134.0 (*Ar*), 139.2 (*C*H=CH$_2$), 139.9 (*Ar*), 144.5 (*Ar*), 170.5 (-*C*OO-), 189.5 ppm (-*C*HO).

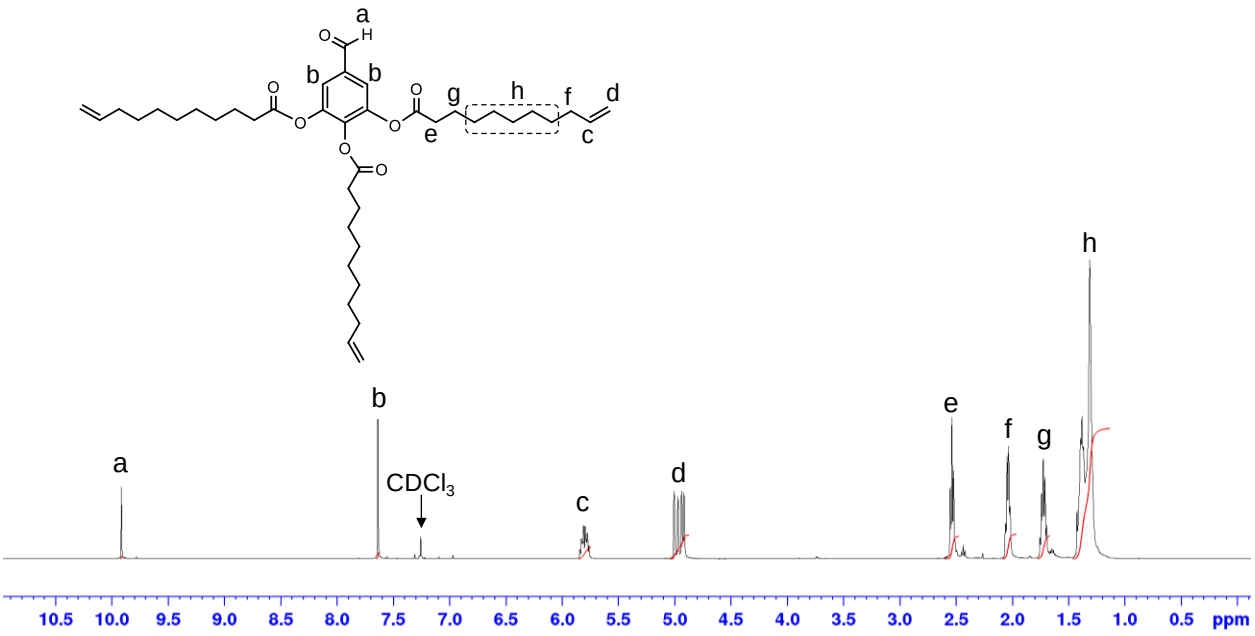

Figure S7. ^{1}H NMR spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (**CL**)

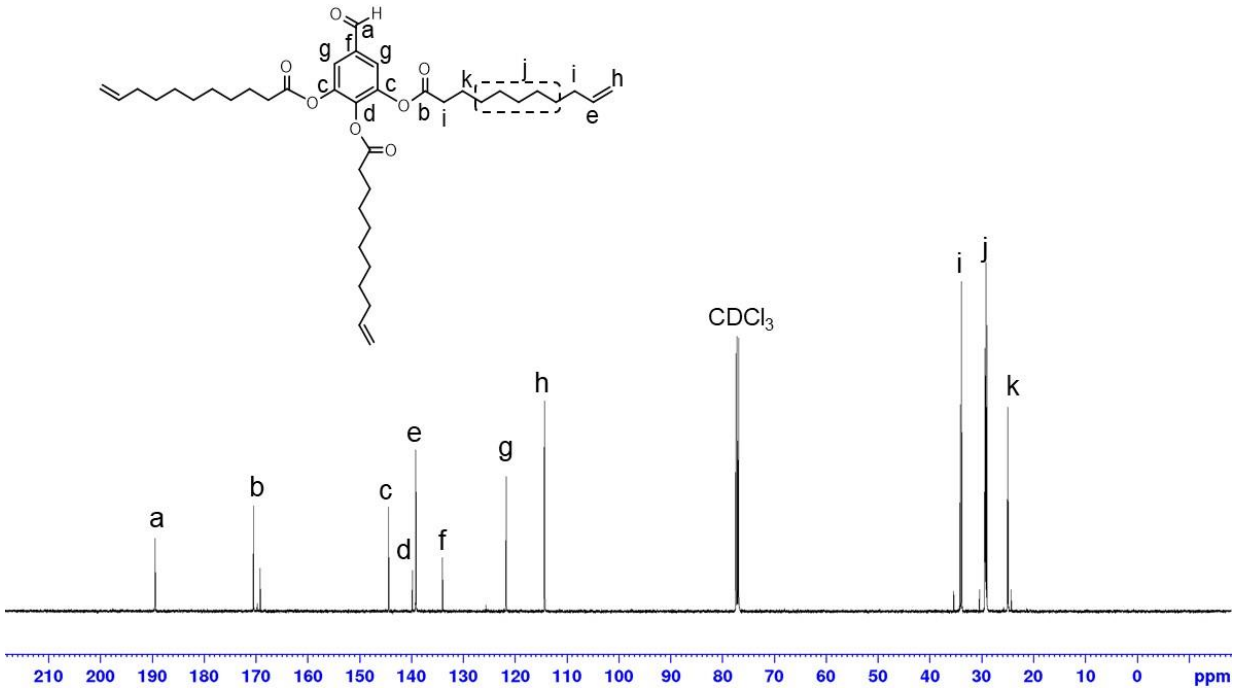

Figure S8. ^{13}C NMR spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (**CL**)

Polymer (P1)

P1 (sample run 8). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.33 (CH_2) 1.75-1.79 (CH_2), 2.03-2.07 (CH_2CH=CH-), 2.55-2.58 (-CH_2COO-), 3.37-3.38 (Ar-CH_2), 3.81 (OCH_3), 5.39-5.67 (-C*H*=C*H*-), 6.15-6.44 (Ar-CH$_2$C*H*=CH-), 6.75-6.79 (C*H*), 6.93-6.94 ppm (C*H*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 25.1 (*C*H$_2$), 26.8 (*C*H$_2$), 29.0 (*C*H$_2$), 29.1 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 32.6 (*C*H$_2$), 33.9 (*C*H$_2$), 34.1 (*C*H$_2$), 39.1 (*C*H$_2$), 55.9 (O*C*H$_3$), 112.8 (*C*H), 120.7 (*C*H), 122.6 (*C*H), 128.6 (Ar-CH$_2$*C*H=CH-), 132.5 (Ar-CH$_2$CH=C*H*-), 138.2 (*C*), 138.9 (-*C*O-), 151.0 (*C*), 172.1 ppm (-*C*OO-).

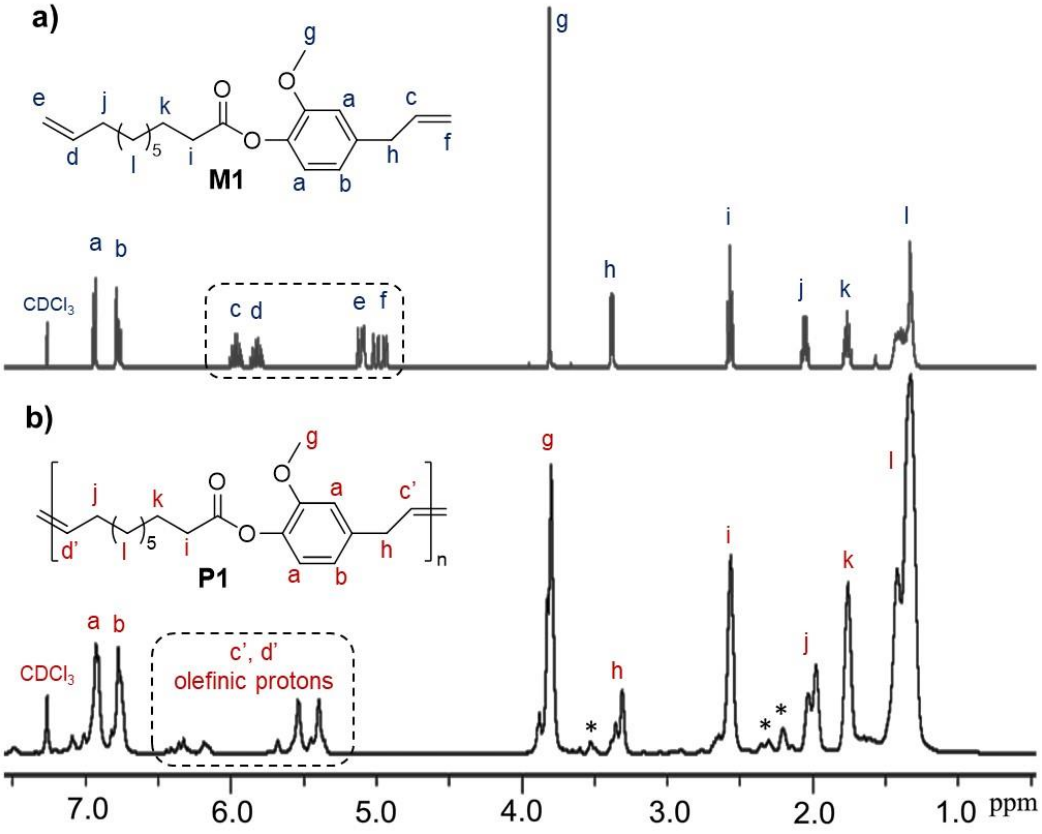

Figure S9. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for (a) monomer (**M1**) and (b) polymer (**P1**)

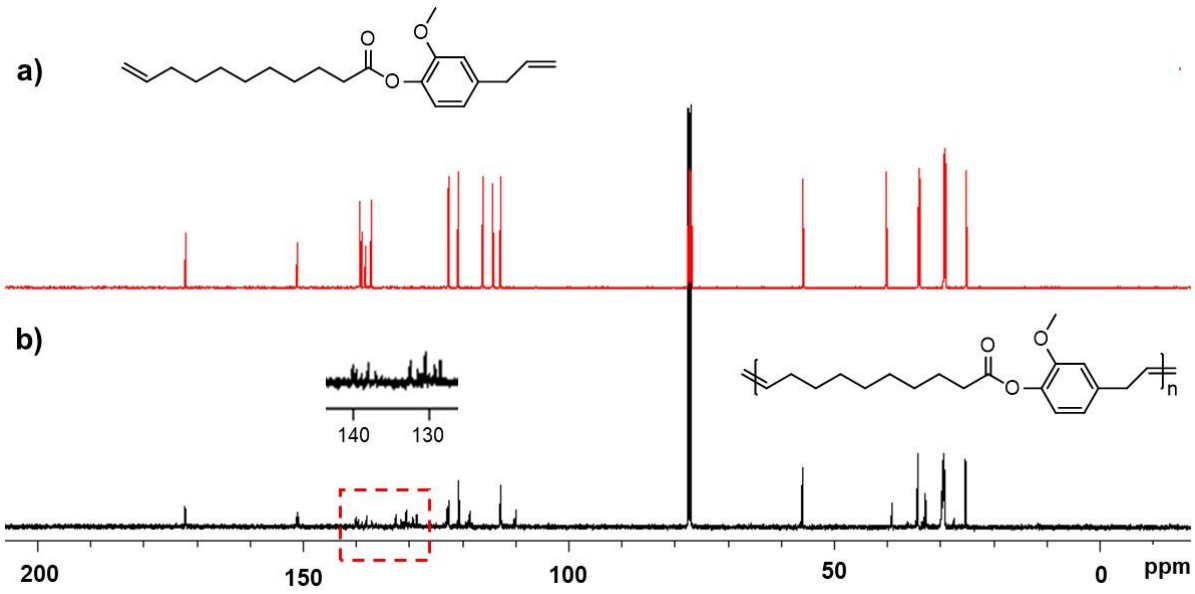

Figure S10. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) for (a) monomer (**M1**) and (b) polymer (**P1**)

Polymer PL1

PL1 (sample run 24). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.32 (C*H*$_2$) 1.75 (C*H*$_2$), 1.97-2.03 (C*H*$_2$CH=CH-), 2.56 (COOC*H*$_2$-), 3.31-3.35 (Ar-C*H*$_2$-), 3.80 (OC*H*$_3$), 5.36- 5.68 (-C*H*=C*H*-), 6.18-6.44 (Ar-CH$_2$C*H*=CH-), 6.77 (CH), 6.92 (C*H*), 7.64 (C*H*), 9.92 ppm (-CO*H*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 25.2 (*C*H$_2$), 26.8 (*C*H$_2$), 29.0 (*C*H$_2$), 29.1 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 32.6 (*C*H$_2$), 33.9 (*C*H$_2$), 34.1 (*C*H$_2$), 39.1 (*C*H$_2$), 55.9 (O*C*H$_3$), 112.8 (*C*H), 120.7 (*C*H), 122.6 (*C*H), 128.6 (Ar-CH$_2$*C*H=CH-), 132.5 (Ar-CH$_2$CH=*C*H-), 138.2 (C), 138.9 (*C*), 144.5 (*C*), 151.2 (*C*), 170.5 (-COO-crosslinker), 172.2 (-COO-), 189.5 ppm (-*C*OH).

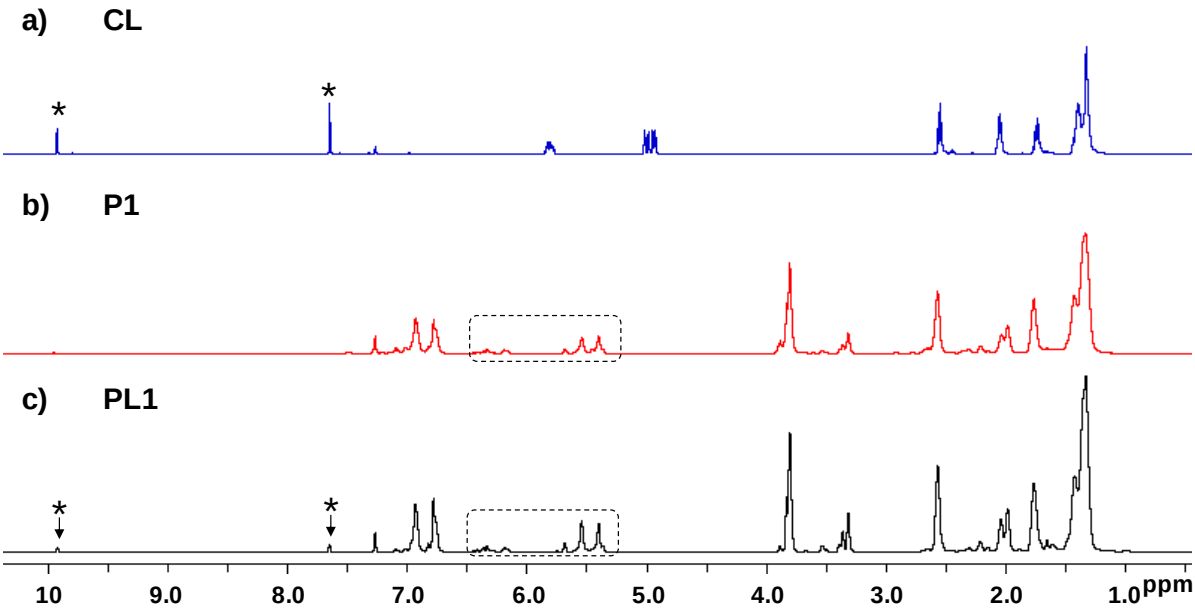

Figure S11. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for (a) crosslinker (**CL**), (b) the resultant polymer (**P1**) prepared by ADMET polymerization of **M1** (run 8), and (c) resultant polymer (**PL1**) prepared by the polymerization of **M1** in the presence of **CL** (5.0 mol%, sample run 24)

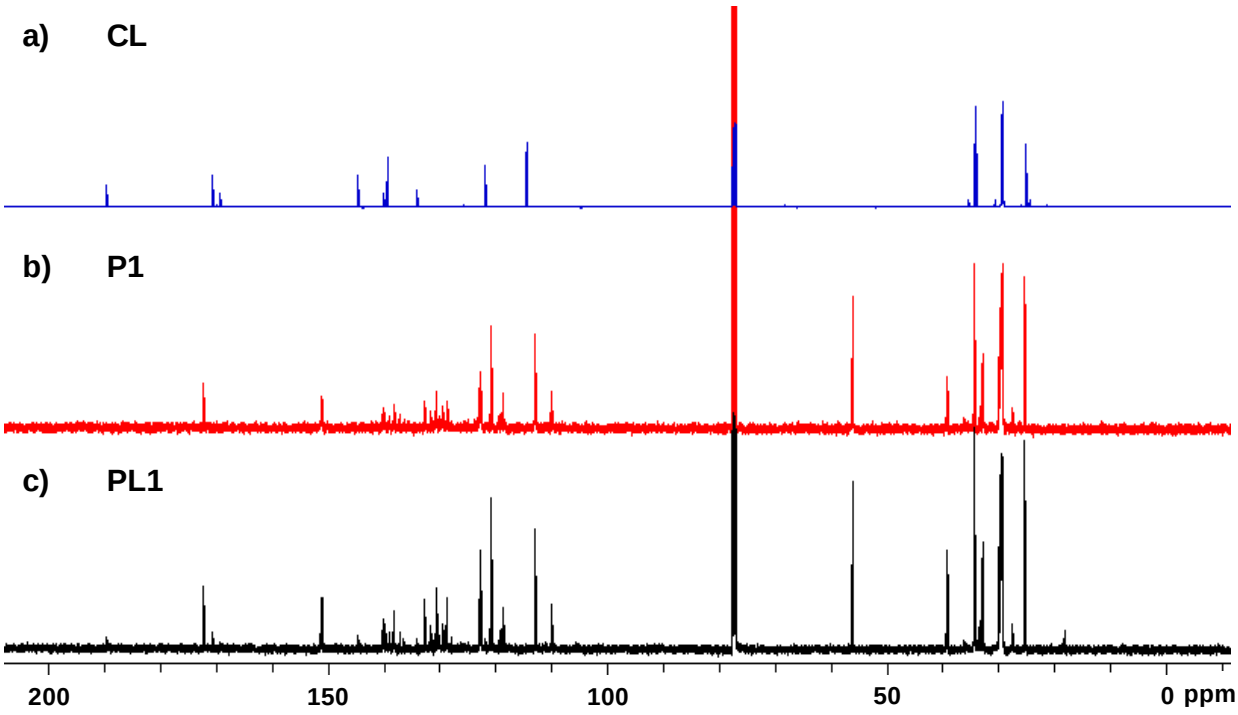

Figure S12. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) for (a) crosslinker (**CL**), (b) the resultant polymer (**P1**) prepared by ADMET polymerization of **M1** (run 8), and (c) resultant polymer (**PL1**) prepared by the polymerization of **M1** in the presence of **CL** (5.0 mol%, sample run 24)

Polymer (P2)

P2 (sample run 14). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.27-1.28 (CH_2), 1.38-1.41 (CH_2), 1.60-1.63 (CH_2), 1.95-2.04 (CH_2CH=CH-), 2.26-2.29 (-CH_2COO-), 4.06 (-COOCH_2-), 5.33-5.42 ppm (-C*H*=C*H*-). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 25.2 (*C*H_2), 25.9 (*C*H_2), 28.3 (*C*H_2), 29.2 (*C*H_2), 29.3 (*C*H_2), 29.4 (*C*H_2), 29.5 (*C*H_2), 32.3 (*C*H_2), 32.7 (*C*H_2), 32.8 (*C*H_2), 34.5 (*C*H_2), 64.3 (-COO*C*H_2-), 130.4 (-*C*H=*C*H-), 174.1 ppm (-*C*OO-).

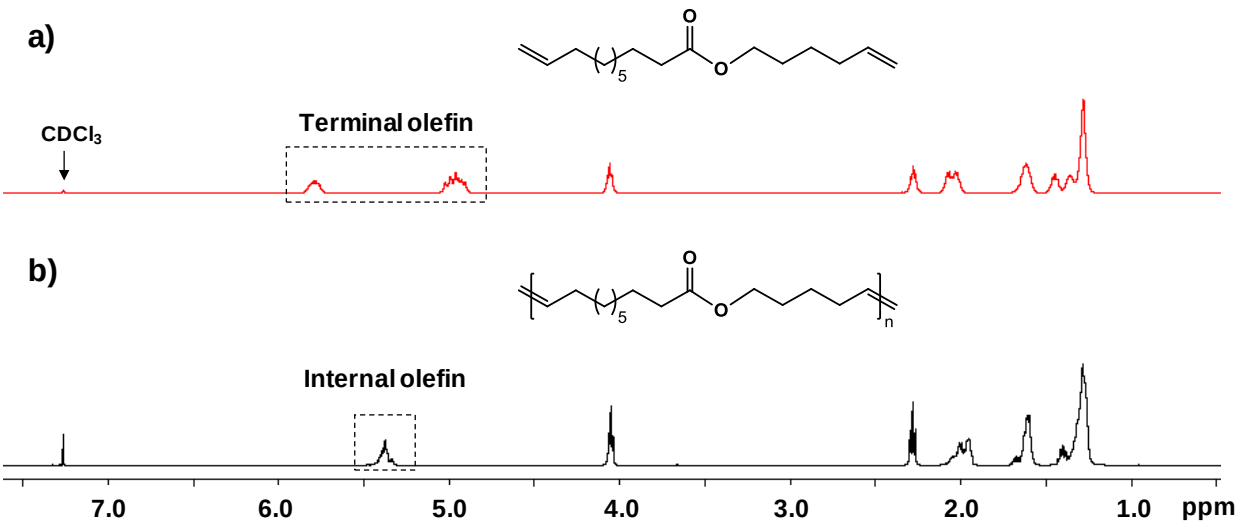

Figure S13. ^{1}H NMR spectrum (in $CDCl_3$ in 25 ºC) for (a) monomer (**M2**) and (b) polymer (**P2**)

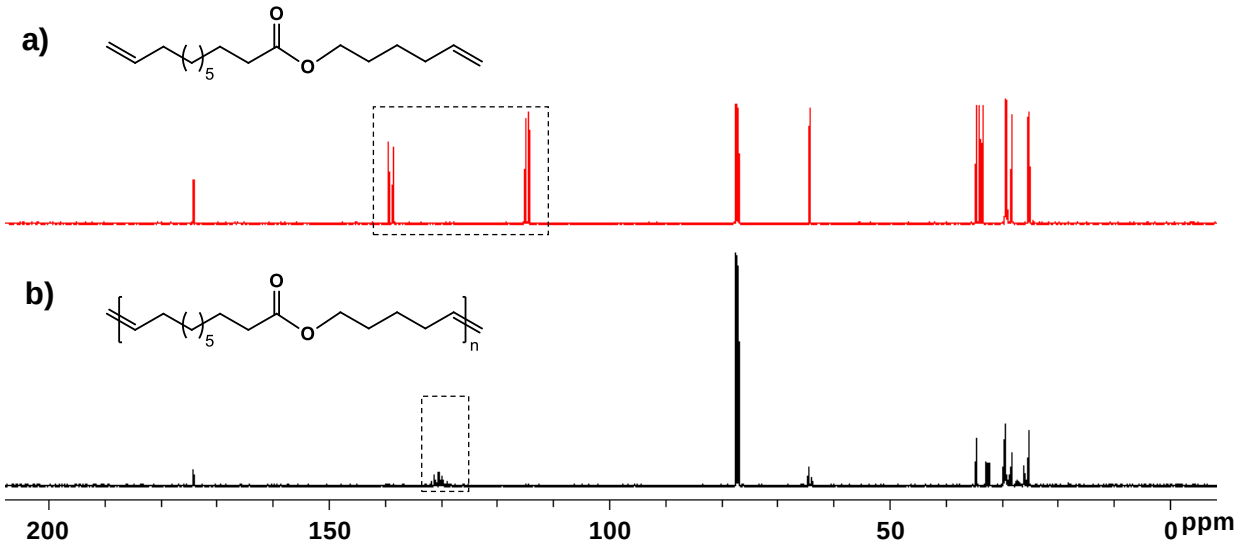

Figure S14. ^{13}C NMR spectrum (in $CDCl_3$ in 25 ºC) for (a) monomer (**M2**) and (b) polymer (**P2**)

Polymer P3

P3 (sample run 19). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.29 (C*H*$_2$), 1.61 (C*H*$_2$), 1.96 (C*H*$_2$-CH=CH), 2.28 (-C*H*$_2$COO-), 4.05 (-COOC*H*$_2$-), 5.38 ppm (-C*H*=C*H*-). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 25.2 (*C*H$_2$), 26.1 (*C*H$_2$), 28.8 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$), 29.9 (*C*H$_2$), 32.7 (*C*H$_2$), 34.5 (*C*H$_2$), 64.5 (-COO*C*H$_2$-), 130.5 (-*C*H=*C*H-), 174.1 ppm (-*C*OO-).

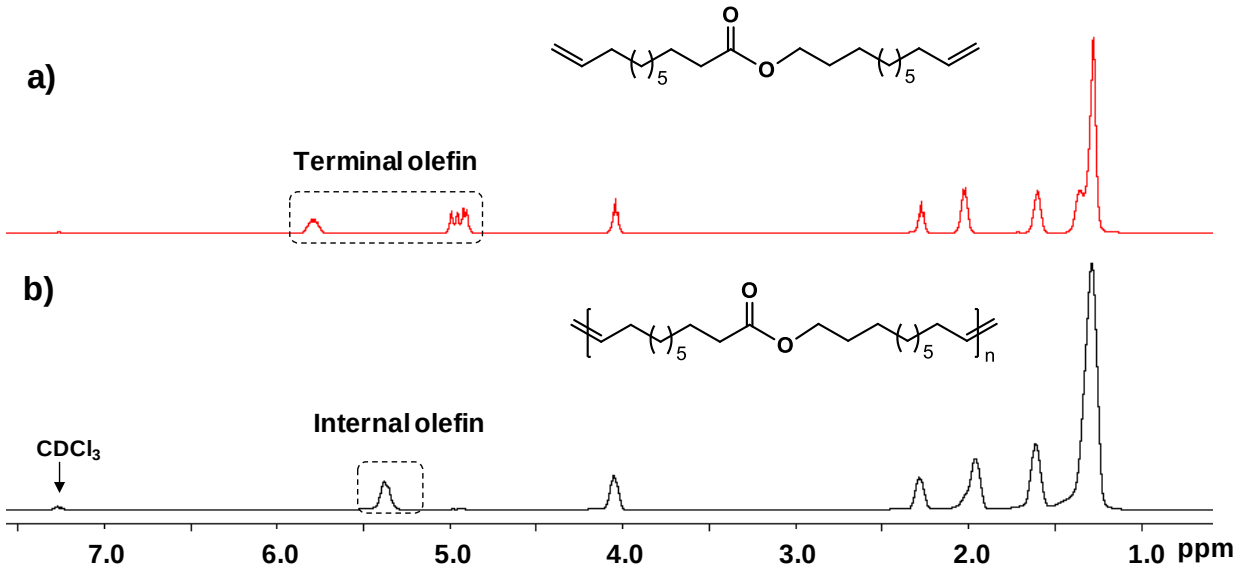

Figure S15. ^{1}H NMR spectrum (in $CDCl_3$ in 25 ºC) for (a) monomer (**M3**) and (b) polymer (**P3**)

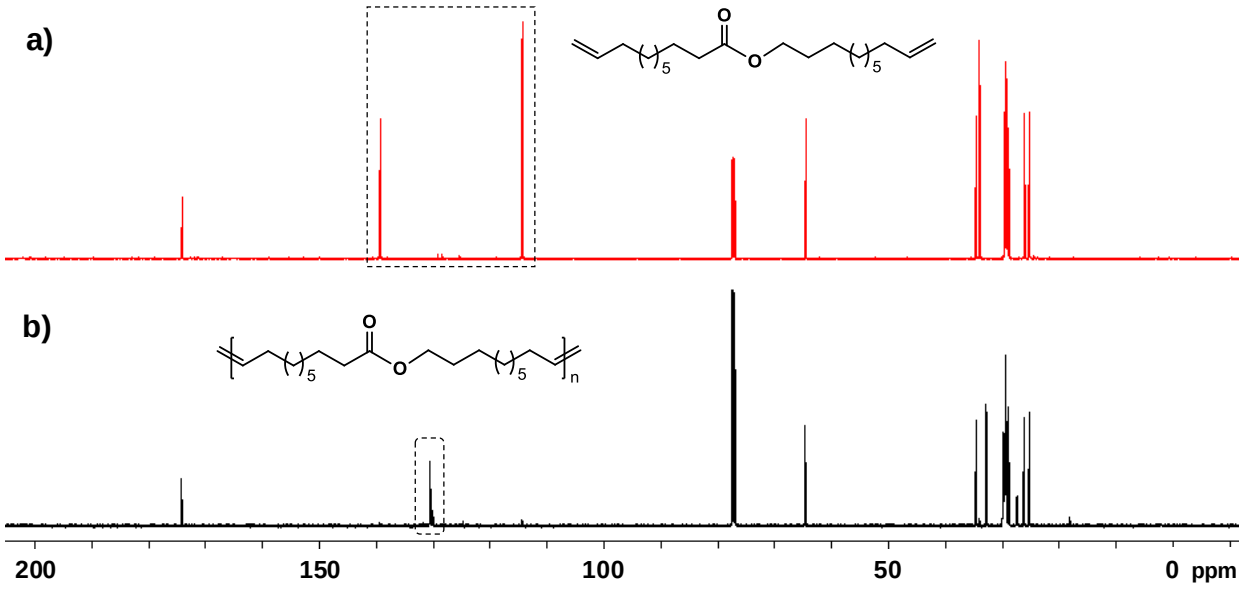

Figure S16. ^{13}C NMR spectrum (in $CDCl_3$ in 25 ºC) for (a) monomer (**M3**) and (b) polymer (**P3**)

(ii) Atmospheric pressure chemical ionization (APCI) mass spectra of monomers and crosslinker

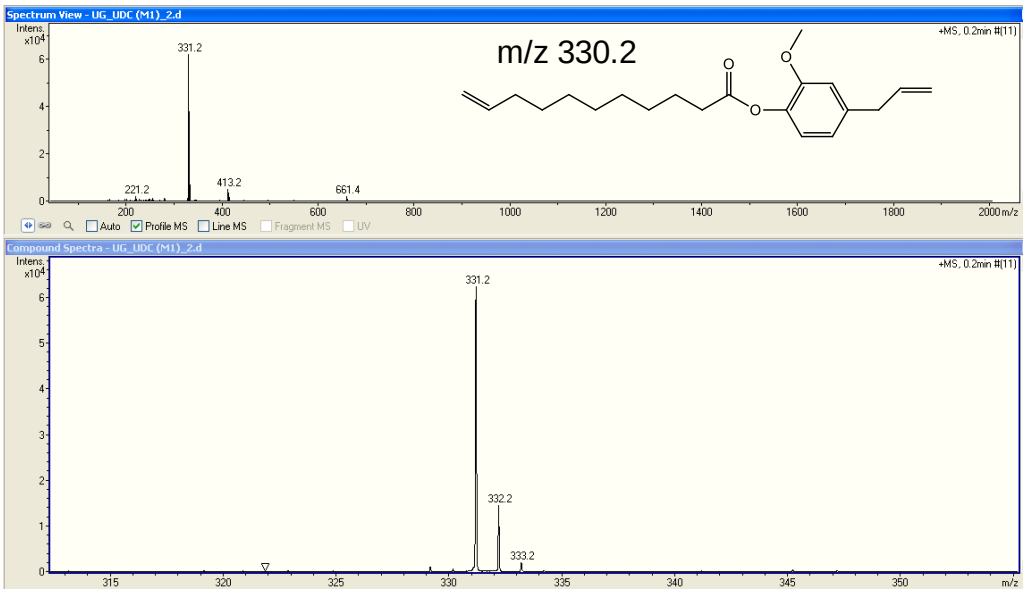

Figure S17. APCI mass spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate **(M1)**

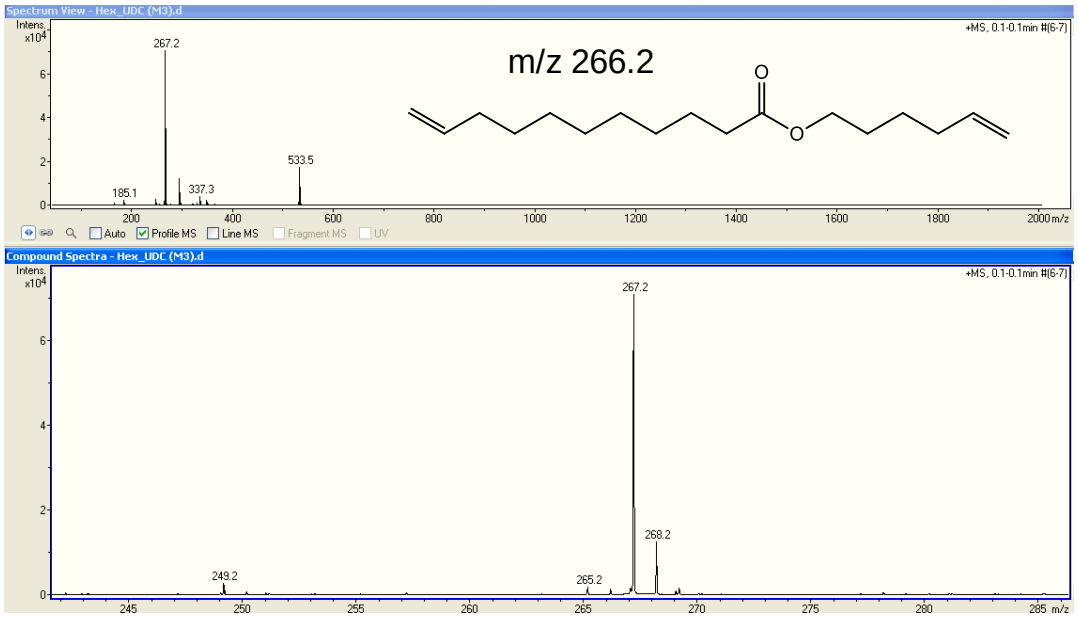

Figure S18. APCI mass spectrum of 5-hexen-1-yl 10-undecenoate **(M2)**

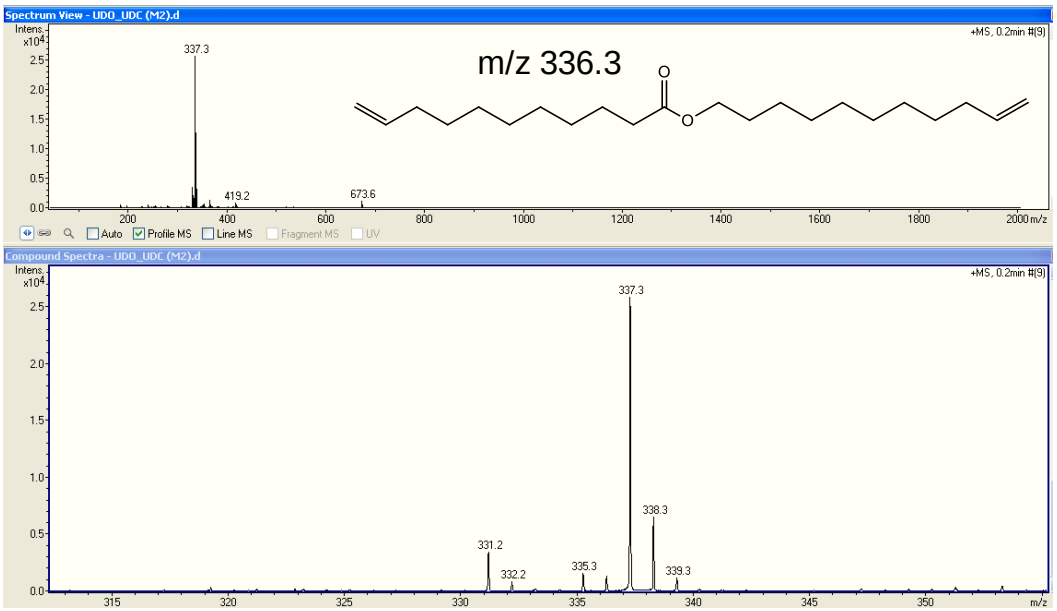

Figure S19. APCI mass spectrum of 10-undecen-1-yl 10-undecenoate **(M3)**

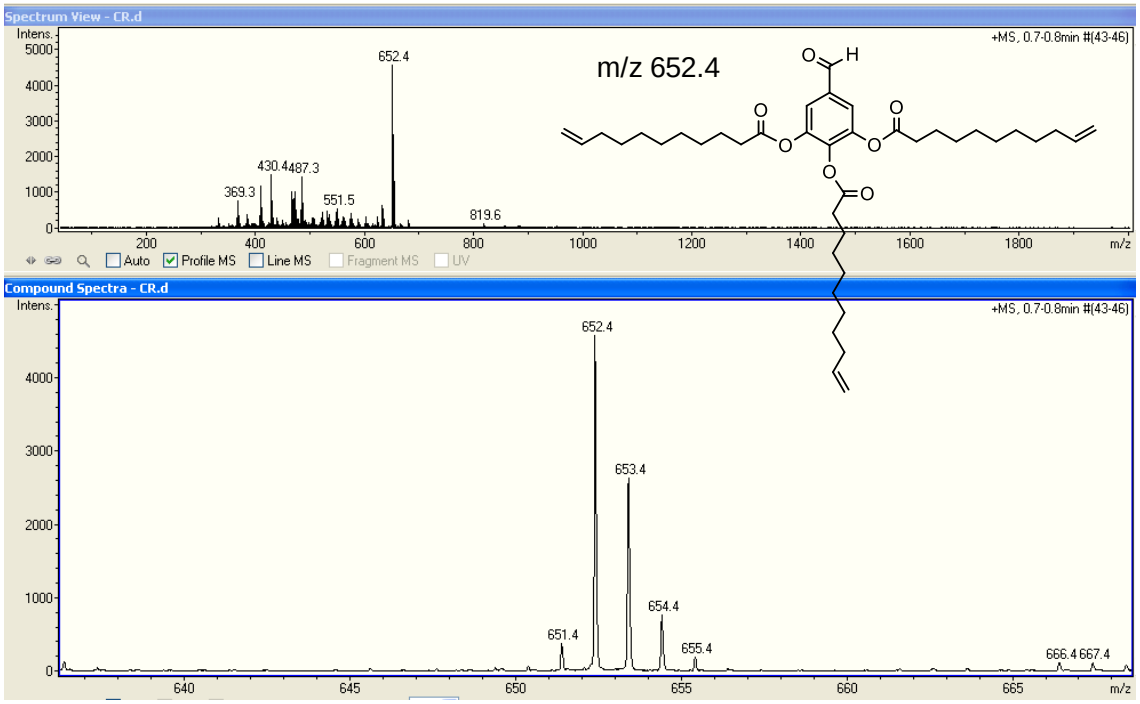

Figure S20. APCI mass spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) **(CL)**

(iii) Selected GPC traces and DSC thermograms of polymers

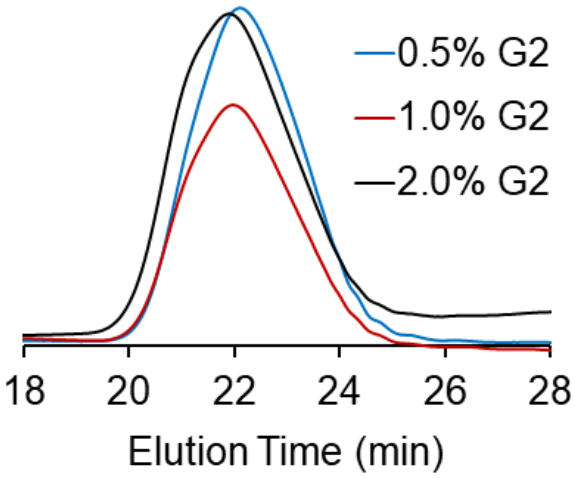

Figure S21. GPC traces of polymers **P2** in ADMET polymerization under effect of different **G2** loading

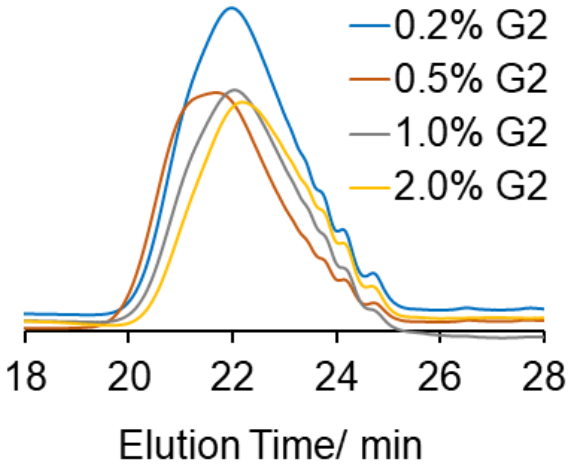

Figure S22. GPC traces of polymers **P3** in ADMET polymerization under effect of different **G2** loading

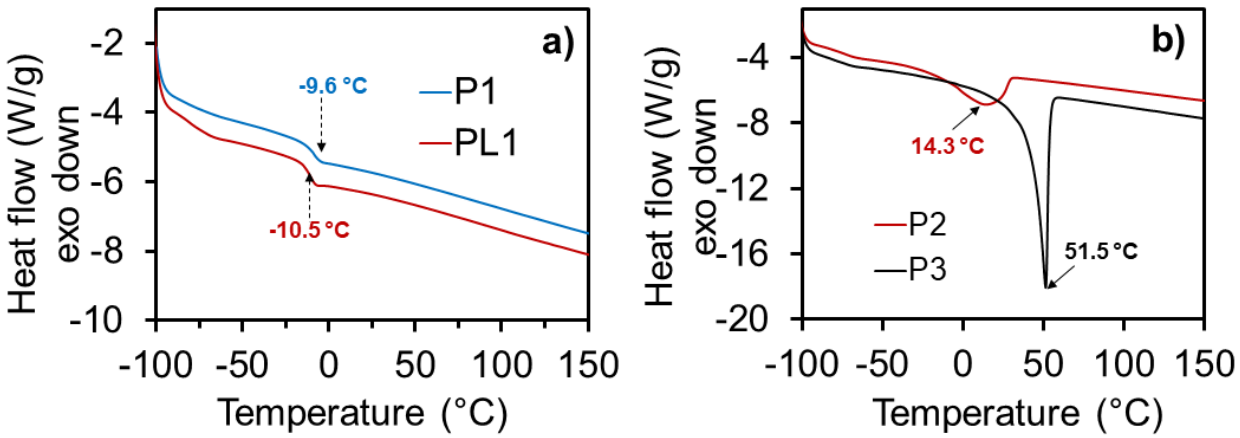

Figure S23. DSC thermograms (exo down) for (a) polymers **P1** (sample run 8), **PL1** (sample run 24) and (b) polymers **P2** (sample run 14)**, P3** (sample run 19), second heating cycle at a heating/cooling rate of 10 °C min^{-1}